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Rudolph A. Marcus

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Semiclassical Theory for Collisions Involving Complexes (Compound State Resonances) and for Bound State Systems†

BY R. A. MARCUS

Department of Chemistry, University of Illinois, Urbana, Illinois 61801

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Semiclassical theory for bound states is discussed and a method is described for calculating the eigenvalues for systems not permitting separation of variables. Trajectory data are supplemented by interpolation to connect open ends of quasi-periodic trajectories. The method is also applied to quasi-bound states.

Previously, semiclassical S-matrix theory has focused on " direct " reactions. Processes involving complexes (compound state resonances) are treated in the present paper and an expression is derived for the S-matrix. Use is made of the above analysis of quasi-bound states and of trajectories connecting those states with open channels. The result deduced for the S-matrix has the expected factorization property, and expressions are given for computing the quantities involved. Some extensions and applications will be described in later papers. An implication for classical trajectory calculations of complexes is noted.

1. INTRODUCTION

A semiclassical S-matrix theory for " direct " inelastic and reactive collisions has been developed in recent papers.[1, 2] (Ref. (3) contains related studies.) On the other hand, many collisions and other processes involve short- or long-lived vibrationally-excited intermediates [4, 5]: unimolecular reactions,[5] molecular beam reactions involving complexes,[6] other bimolecular reactions (e.g., possible at a threshold),[7] and intramolecular energy transfer in general.[8]

In the present paper we consider the dynamics of coupling between open channels and quasi-bound states (" compound state resonances "[9]), and formulate a semiclassical S-matrix theory for such collisions. The theory of direct collisions [1] is first summarized in Section 2. A method utilizing classical mechanical trajectory data is proposed in Section 3 for calculation of eigenvalues of bound states. It is non-perturbative and is directed toward systems for which one cannot separate variables. It is adapted in Section 4 to quasi-bound states.

The principal result for quasi-bound states is given by eqn (4.9), (4.12), (4.16) and (4.17). A method for calculating the quantities is described. One-dimensional (" shape ") resonances, such as those occurring in orbiting, have earlier been treated semiclassically.[10-12]

2. SEMICLASSICAL THEORY OF DIRECT COLLISIONS

The semiclassical wave function $\psi^+(\mathbf{q}, nE)$ is a function of the coordinates, denoted collectively by $\mathbf{q}$, the quantum numbers n, and the total energy E. For direct inelastic collisions, this wave function at large separation distances R is [1]

$$\psi^+(\mathbf{q}, nE) \equiv \langle \mathbf{q}|nE^+\rangle = [A^1 \exp\{iF_2^1\} + A \exp\{i(F_2 - \tfrac{1}{2}\pi)\}] \exp\{il_n\pi/2\}, \qquad (2.1)$$

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where the term with superscript i describes the incoming particles, and the second term is for the outgoing ones.* The A's and F's are functions of $\mathbf{q}$, n and E; $-\pi/2$ is the usual phase loss for a reflection; $l_n\pi/2$ is present by convention, where l_n is the orbital quantum number contributing to n. Units of $\hbar = 1$ are used.

F_2 in (2.1) is a classical mechanical generating function [13] and serves to make a canonical transformation of variables from $\mathbf{q}$, $\mathbf{p}$ to momenta in nE and to conjugate coordinates). Illuminating discussions of the relation between classical canonical transformations (e.g., embodied in $F_2(\mathbf{q}, nE)$) and quantum mechanical unitary transformations (e.g., embodied in $\langle \mathbf{q}|nE^+\rangle$ have been given.[14-16]

F_2^i for a partial wave, when the $\mathbf{q}$'s consist of a radial coordinate R and angle coordinates w, is given by (2.2). [The value when the $\mathbf{q}$'s are conventional coordinates appears later in (4.5).]

$$F_2^i(wR, nE) = -k_nR+2\pi nw, \tag{2.2}$$

The w's are canonically conjugate to $2\pi n$ and are frequently employed for the internal motions.[1, 2, 17-19] Their properties are very convenient and have been summarized in Part IV.[1] nw is an abbreviation for $\Sigma n_j w_j$, the summation being over the various internal degrees of freedom (including orbital, if any).

$F_2(wR, nE)$ is the phase integral calculated from the classical trajectory passing through the cited $\mathbf{q}$ [the point (w, R)], beginning at the given n and E and hence at some initial point (w_0, R_0):

$$F_2(wR, nE) = -k_nR_0+2\pi n w_0+\int_{R_0}^{R} p_R\,\mathrm{d}R+2\pi\int_{w_0}^{w}\bar{n}\,\mathrm{d}w, \tag{2.3}$$

where $\bar{n}$ is the instantaneous n along the path.

The amplitude A in semiclassical solutions can be evaluated either by flux conservation [1, 20-22] or by normalization to a δ-function.[2, 15-16] When normalized to $\delta(n-n')[2\pi\delta(E-E')]$ it is the determinant †

$$A = |\partial^2 F_2/\partial\alpha\partial q|^{\frac{1}{2}} \tag{2.4}$$

where the α's are E and (since $\hbar = 1$) $2\pi n$. One finds from (2.2)-(2.4) that

$$A^i = v_n^{-\frac{1}{2}}, \qquad A = v^{-\frac{1}{2}}|\partial w_0/\partial w|^{\frac{1}{2}}, \tag{2.5}$$

where v_n and v denote the magnitude of the initial and final radial velocity for the trajectory specified by the final point (wR) and the initial momenta present in nE.

The semiclassical S-matrix S_{mn} can be defined via the expression for ψ^+ at large R:

$$\psi^+(wR, nE) = \sum_m v_m^{-\frac{1}{2}}(\exp\{2\pi i m w\})[\delta_{mn}\exp\{-\mathrm{i}(k_mR-\tfrac{1}{2}l_m\pi)\}- S_{mn}\exp\{\mathrm{i}(k_mR-\tfrac{1}{2}l_m\pi)\}]. \tag{2.6}$$

Comparison of (2.1) and (2.6) yields (Part II, ref. (1))

$$S_{mn} = \int_0^1 |\partial w_0/\partial w|^{\frac{1}{2}}(\exp \mathrm{i}\Delta)\,\mathrm{d}w \quad \text{(to be stationary phased)}, \tag{2.7}$$

using the fact that only the stationary phase points contribute (whence $v = v_m$).[1] Δ is given by

$$\Delta = F_2(wR, nE)-F_2^i(wR, mE)+\tfrac{1}{2}(l_m+l_n+1)\pi. \tag{2.8}$$

* The wave function given by eqn (2.1)-(2.6) is for a volume element $\mathrm{d}\mathbf{q}$. If the volume element is $g^{\frac{1}{2}}\,\mathrm{d}\mathbf{q}$, e.g., $R^2\,\mathrm{d}R\,\mathrm{d}w$,[1] then (2.1) and (2.6) are multiplied by $g^{-\frac{1}{2}}$, e.g., R^{-1}.

† This is equivalent in (2.5) to the normalization used in ref. (1), where each A was normalized to unit radial flux at a given R.

A stationary phase evaluation of (2.7) yields [1]

$$S_{mn} = \sum_{w'} (-i\partial\bar{n}/\partial w_0)^{-\frac{1}{2}} \exp\{i[F_4(mE, nE) + \tfrac{1}{2}(l_m + l_n + 1)\pi]\} \tag{2.9}$$

evaluated at $\bar{n} = m$.

The summation is over stationary phase points w', i.e., over the one or several trajectories leading from the initial momenta in nE to the final momenta in mE. (The Riemann sheet discussion in Section 3 and 4 provides an understanding of the fact that several trajectories lead from nE to mE, namely one per sheet.) F_4 is a generator[13] for a canonical transformation from nE to mE, and was denoted by Δ', apart from the π-terms, in ref. (1).

$$F_4(mE, nE) = -\int_{-k_n}^{k_m} R\, dp_R - 2\pi \int_n^m w\, d\bar{n} = -\int \mathbf{q}\, d\mathbf{p}. \tag{2.10}$$

A uniform approximation [1, 2] of (2.7) can be made. It usually involves Airy functions and has wider validity than the stationary phase value, (2.9).[1, 2]

The amplitude A in (2.5) becomes infinite on certain surfaces (" caustics "). This infinity in A is detected by the intersection there of neighbouring trajectories. (E.g., see later, " surfaces " AB, BC, CD and DA in fig. 1): the resulting vanishing of the " cross-sectional area " between the trajectories causes the amplitude A to become infinite to " conserve probability flux." In such cases one can still usually use (2.7) to obtain a stationary phase or uniform approximation for S_{mn}, since the stationary phase points are themselves usually nonsingular.

To have a useful integral expression for S_{mn} one can change the coordinate representation to one which is sometimes singularity-free, by a canonical transformation (Part III of ref. (1)) from wR to $\bar{w}\tau$, where the $\bar{w}$ are constant and τ is a time variable. This representation leads to the same result as (2.7), but with ∂w amd dw replaced by $\partial\bar{w}$ and $d\bar{w}$, and with Δ having an added term $2\pi(\bar{n} - m)\bar{w}$. The uniform and stationary phase values of the new expression agree exactly with those of (2.7)-(2.9), but the new integral is now sometimes also of particular use when asymptotic evaluation methods become poor. The form of this integral expression had been predicted by intuitive arguments.[2]

3. SEMICLASSICAL TREATMENT OF EIGENVALUE PROBLEMS

To obtain the phase $F_2(\mathbf{q}, n)$ of the wave function for a bound state at a point $\mathbf{q}$, one may integrate along a trajectory, as in (2.3). Except in the case of degeneracy, accidental or intrinsic, this trajectory does not close on itself, i.e., is not periodic.

Moser [23] and Arnold [23] have proved an important theorem for celestial mechanics and thereby for the present nonlinear mechanics. Under certain conditions for systems not permitting (or permitting) separation of variables, the motion is quasi-periodic (multiply-periodic) rather than ergodic. That is, the $\mathbf{p}$'s amd $\mathbf{q}$'s can be represented as functions of time by Fourier series, e.g., $\sum_{m_1 \ldots m_N} a_{m_1 \ldots m_N} \exp\{i \sum_{i=1}^{N} 2\pi m_i \nu_i t\}$, where the m's denote the integers from $-\infty$ to ∞ and where the coefficients a decrease exponentially with $(|m_1| + \ldots + |m_N|)$.[23] The contrast between ergodic and quasi-periodic is seen in fig. 1: the former would occupy the whole space within the line of constant energy, while the other would be more confined spatially. In a nondegenerate system, N is the number of degrees of freedom. The ν_i are the frequencies of the true angle variables w_i for this problem, i.e., those canonically conjugate to the actions,

$2\pi n_i$, the classical counterparts of the quantum numbers. Hamilton's equations of motion yield

$$\mathrm{d}(2\pi n_i)/\mathrm{d}t = -\partial H(n)/\partial w_i = 0, \quad \mathrm{d}w_i/\mathrm{d}t = \partial H(n)/\partial(2\pi n_i) = \nu_i(n). \tag{3.1}$$

Quasi-periodicity implies that there is a canonical transformation from $(\mathbf{q}, \mathbf{p})$ to $(w, 2\pi n)$ and hence a generating function $F_2(\mathbf{q}, n)$ * for this transformation. In turn, $F_2(\mathbf{q}, n)$ defines a congruence of trajectories, directed along ∇F_2. Later, F_2 will be the phase in a semiclassical wave function, each " surface " of constant phase serving as a wave front and the trajectories serving as rays along the normal to the front.

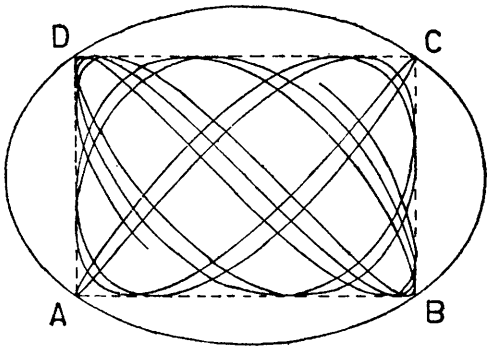

FIG. 1.—" Box-like " orbit formed by a simple trajectory in a bound or quasi-bound state. (The actual figure was made for two uncoupled oscillators, using conventional coordinates.) Caustics are AB, BC, CD, DA. The elliptical curve is a constant energy curve, with energy equal to the total energy.

In the nondegenerate situation depicted in fig. 1 a single trajectory, for the case of two degrees of freedom, generates four congruences of rays, corresponding to the four possible algebraic signs of the two components of the momentum $\mathbf{p}$, as seen in fig. 1 and as emphasized in fig. 2 and (in Appendix) fig. 4. The corresponding ∇F_2 $(= \mathbf{p})$

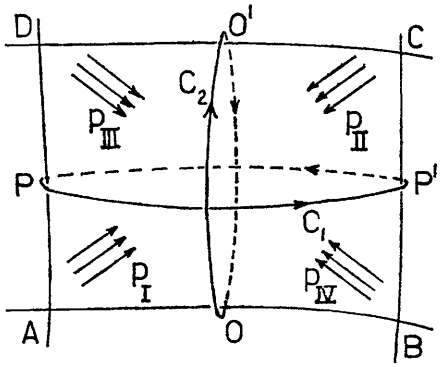

FIG. 2.—Congruences of rays present in fig. 1, each corresponding to a branch (Riemann sheet) of the function $\mathbf{p}(\mathbf{q})$.

then has four branches (Riemann sheets).[20] [When there are N coordinates instead of 2 there are 2^N branches.] The rays in fig. 1 do not cross when they are on the same sheet, except at the boundaries, i.e., at the caustics AB, BC, CD, DA.

* The symbol $F_2(\mathbf{q}, n)$ is shorthand notation for $F_2(\mathbf{q}, 2\pi n)$. An analogous remark applies to F_2 in Section 2.

The semiclassical wave function is a linear combination of the solutions, $A(\mathbf{q})\exp\{iF_2(\mathbf{q}, n)\}$, one per sheet; F_2 is $\int \mathbf{p}\,d\mathbf{q}$. In the several-dimensional wave diffraction literature, the formula for connecting such asymptotic expansion terms is found by assuming a local separation of variables near the caustic and solving the local problem exactly.[24] The local solution usually involves the Airy function and its derivative. When this procedure is applied to the present problem in the vicinity of caustics AB and AD, near point A, one obtains (3.2) for the case of two vibrations. (It is easily generalized to N-coordinates, and then has 2^N terms.) Each sheet of F_2 is described by a Roman numeral:

$$\psi(\mathbf{q}, \mathrm{P}) = C|\partial^2 F_2^{\mathrm{I}}/\partial q\partial\alpha|^{\frac{1}{2}}[(\exp\{i(F_2^{\mathrm{I}}-\tfrac{1}{2}\pi)\}+(\exp\{i(F_2^{\mathrm{II}}+\tfrac{1}{2}\pi)\})]+ C|\partial^2 F_2^{\mathrm{III}}/\partial q\partial\alpha|^{\frac{1}{2}}[(\exp\{iF_2^{\mathrm{III}}\})+(\exp\{iF_2^{\mathrm{IV}}\})] \tag{3.2}$$

where

$$F_2^{\gamma} \equiv \int_A^q \mathbf{p}_\gamma\,d\mathbf{q}, \qquad (\gamma = \mathrm{I, II, III, IV}) \tag{3.3}$$

and

$$\mathbf{p}_{\mathrm{II}} = -\mathbf{p}_{\mathrm{I}}, \qquad \mathbf{p}_{\mathrm{IV}} = -\mathbf{p}_{\mathrm{III}}. \tag{3.4}$$

α denotes $2\pi n_1$ and $2\pi n_2$; C is a normalization constant. The pre-exponential factors, which are absolute values of the determinants, are equal in the region near A. One sees from (3.4) that congruence II(IV) is related to I(III) by time-reversal.

If one similarly obtains a local solution in the vicinity of D, and uses it to obtain the connection formula relating the $(A\exp iF_2)$'s, the resulting ψ is similar to (3.2), but with A replaced by D and with a different arrangement of the $\pi/2$'s, namely 0, 0, $-\pi/2$, $\pi/2$ for branches I to IV. Since ψ is single-valued these two solutions can differ at most by a multiplicative constant. A further analysis (Appendix) then establishes (3.5). A similar comparison of (3.2) with the ψ resulting from a local solution near B yields (3.6):

$$2\pi(n_2+\tfrac{1}{2}) = \oint_{C_2} \mathbf{p}\,d\mathbf{q} = \int_{\mathrm{O}}^{\mathrm{O}'} \mathbf{p}_{\mathrm{I}}\,d\mathbf{q} + \int_{\mathrm{O}'}^{\mathrm{O}} \mathbf{p}_{\mathrm{III}}\,d\mathbf{q} \tag{3.5}$$

$$2\pi(n_1+\tfrac{1}{2}) = \oint_{C_1} \mathbf{p}\,d\mathbf{q} = \int_{\mathrm{P}}^{\mathrm{P}'} \mathbf{p}_{\mathrm{I}}\,d\mathbf{q} + \int_{\mathrm{P}'}^{\mathrm{P}} \mathbf{p}_{\mathrm{III}}\,d\mathbf{q} \tag{3.6}$$

where O, O′, P, P′ are arbitrary points on their respective caustics, as in fig. 2.

It may be emphasized for this derivation that the local separation of variables near a caustic is used only to obtain the connection formulae of the $(A\exp iF_2)$'s. The global nature of the $(A\exp iF_2)$'s as solutions, for points not near caustics, is the principal tenet (asymptotic expansion) of semiclassical theory.

Eqn (3.5) and (3.6) have been obtained earlier by a different argument[20]: each $(A\exp iF_2)$ term was assumed to be single-valued and A was allowed to vary on passage through a caustic. (This appears to be a type of phase integral argument.) The present discussion and that in Section 4 avoids a phase integral approximation, though the latter frequently suffices.

F_2 satisfies the Hamilton-Jacobi partial differential equation and the method of characteristics (classical trajectories) is a convenient method for solving it. However, that method is not the only one. Thus, it should be emphasized that the $\int \mathbf{p}\,d\mathbf{q}$'s need not be along dynamical trajectories, that is, along a ray congruence. In fact, in the case of a nondegenerate system the motion is not periodic and so one cannot compute the C_1 and C_2 path integrals merely by integration along classical trajectories.

Instead, one can use an " interpolation " of the exact trajectory data to close the ends of an open ended path. For example, the $\int \mathbf{p}\,d\mathbf{q}$ data obtained from the single trajectory can be represented by a Fourier series. One may then use that series to join two ends of a trajectory and so compute $\oint \mathbf{p}\,d\mathbf{q}$ along the two independent paths. Fourier series, suitably chosen to avoid the " small divisor " problem when necessary, have been extensively used in the astronomical literature.[25] Fig. 1 describes an orbit which has been termed " box-like " in the computer-simulated stellar dynamics literature.[26] Other classes of orbits exist (" shell-like," " tube-like "),[26] readily understood physically, and can be analogously treated.

The need for supplementing trajectory data by interpolation for calculation of $\oint \mathbf{p}\,d\mathbf{q}$ has been missed, incidentally, by a number of authors,[27] who accordingly but incorrectly insisted on periodic dynamical trajectories. (The classical Feynman propagator, with its usual dynamical associations, was used as a starting point.) Two other approaches should also be recalled: perturbation theory [18, 28] and a proposed mapping of the nonseparable problem onto a separable one.[29] Quasi-periodicity implies incidentally, that there exists a canonical transformation for a mapping of the nonseparable one onto a separable one, since the problem in (3.1) has become separable.

4. SEMICLASSICAL THEORY OF COMPOUND-STATE RESONANCES

The description of the quasi-bound (q-b) state, like the bound state, involves caustics. The two states differ, in that the q-b state is connected via (real or complex) trajectories to other states, e.g., to open collision channels. We consider, by way of example, the situation depicted in fig. 3, where AB, BC, DC and DA are caustics bounding the q-b state. The semiclassical wave function for collisions involving compound-state resonances is constructed below so as to satisfy the boundary conditions at $R = \infty$, and in the vicinity of the various caustics.

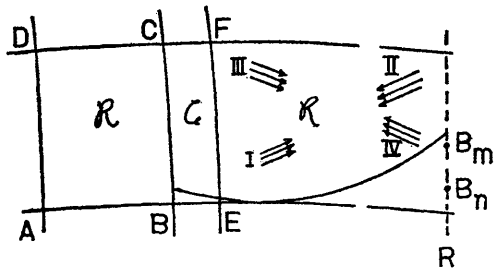

FIG. 3.—Schematic picture of caustics AB, BC, CD, DA bounding the quasi-bound state, and caustic EF " shielding " the state from the open channels at large R. B_n and B_m are vibrational turning points for states nE and mE at large R. A dynamical trajectory to caustic BC is indicated. When EF and BC are real-valued caustics, **P** is real in regions $\mathscr{R}$ and complex in $\mathscr{C}$. All arrows in *this* figure refer to motion *at the dotted line.*

For simplicity of presentation the case where entrance and exit from the q-b state occur mainly at one of the caustics BC in fig. 3, will be considered. Quantum mechanically, the region in the vicinity of such a caustic would then be the one contributing most to the matrix elements coupling the q-b state to the open channels. Fig. 3 is schematic: the q-b state and open channels are separated by " caustics ", but spatially the two regions may overlap. Again, like the bound state, more complicated examples exist.

As in Section 3 a solution based on local separation of variables near A, to find the connection formula, yields (3.2). Comparison with a solution determined near D yields (3.5). A local separation of variables is made in a segment near caustic EB, followed by use of the one dimensional solution for the coordinate normal to EB and the two turning-point one dimensional solution [11] for the curvilinear coordinate parallel to EB. (The two turning points occur on EF and on BC.) When the latter is fitted to the solution (3.2) one obtains the desired connection formula, whence a standing wave solution $\langle \mathbf{q}|n_2E\rangle$ for the q-b state $|n_2E\rangle$ is found to be

$$\langle \mathbf{q}|n_2E\rangle = 2^{\frac{1}{2}}|\partial^2 F_2^{\mathrm{I}}/\partial q\partial\alpha|^{\frac{1}{2}}(\exp\{iG^{\mathrm{I}}\}+\exp\{iG^{\mathrm{II}}\})+ 2^{\frac{1}{2}}|\partial^2 F_2^{\mathrm{III}}/\partial q\partial\alpha|^{\frac{1}{2}}(\exp\{iG^{\mathrm{III}}\}+\exp\{iG^{\mathrm{IV}}\}) \quad (4.1)$$

where

$$G^{\mathrm{I}} = F_2^{\mathrm{I}}+\delta_{rs}-\tfrac{1}{2}\phi_s-\tfrac{1}{2}\pi, \qquad G^{\mathrm{II}} = F_2^{\mathrm{II}}-\delta_{rs}+\tfrac{1}{2}\phi_s+\tfrac{1}{2}\pi \quad (4.2)$$

$$G^{\mathrm{III}} = F_2^{\mathrm{III}}+\delta_{rs}-\tfrac{1}{2}\phi_s, \qquad G^{\mathrm{IV}} = F_2^{\mathrm{IV}}-\delta_{rs}+\tfrac{1}{2}\phi_s$$

$$F_2^{\gamma} = \int_E^q \mathbf{p}_\gamma\, d\mathbf{q} \qquad (\gamma = \mathrm{I}, \ldots, \mathrm{IV}). \quad (4.3)$$

The $\mathbf{p}_\gamma$'s are related as in (3.4), and so $F^{\mathrm{II}} = -F_2^{\mathrm{I}}$ and $F_2^{\mathrm{IV}} = -F_2^{\mathrm{II}}$. Thus, (4.1) is a standing wave solution. δ_{rs} and ϕ_s are independent of n and m and are discussed later. s denotes n_2E.

Eqn (4.1) contains two radially ingoing terms (branches II and IV) whose sum is denoted by $\langle \mathbf{q}|n_2E^{\mathrm{i}}\rangle$, and two radially outgoing terms (branches I and III), whose sum is denoted by $\langle \mathbf{q}|n_2E^{\mathrm{f}}\rangle$, so that $\langle \mathbf{q}|n_2E\rangle$ is the sum of these. Each sum is separately normalized to $\delta(n_2-n_2)[2\pi\delta(E-E')]$ (and hence to unit radial flux).

We turn now to the $\psi^+(\mathbf{q}, nE)$ satisfying the appropriate boundary conditions for a collision. The incident term in (2.1), denoted by $\langle \mathbf{q}|nE^{\mathrm{i}}\rangle$, is given by (4.4) using conventional coordinates,

$$\langle \mathbf{q}|nE^{\mathrm{i}}\rangle = 2^{-\frac{1}{2}}[|\partial^2 F_2^{\mathrm{i,II}}/\partial q\partial\alpha_n|^{\frac{1}{2}}\exp\{iF_2^{\mathrm{i,II}}+\tfrac{1}{4}i\pi\}+ |\partial^2 F_2^{\mathrm{i,IV}}/\partial q\partial\alpha_n|^{\frac{1}{2}}\exp\{iF_2^{\mathrm{i,IV}}-\tfrac{1}{4}i\pi\}]\exp\{il_n\pi/2\}, \quad (4.4)$$

where

$$F_2^{\mathrm{i},\gamma} = \int_{B_n}^q \mathbf{p}_\gamma\, d\mathbf{q} - k_nR \qquad (\gamma = \mathrm{II}, \mathrm{IV}). \quad (4.5)$$

B_n is the vibrational turning point in state nE at the given R (fig. 3). In branch II the vibrational momentum points toward and in branch IV away from B_n. Similarly, the wavefunction $\langle \mathbf{q}|nE^{\mathrm{f}}\rangle$ for an outgoing wave is identical with (4.4)-(4.5) but with II and IV replaced by III and I, respectively. The unperturbed wave function is the sum $\langle \mathbf{q}|nE^{\mathrm{i}}\rangle+\langle \mathbf{q}|nE^{\mathrm{f}}\rangle$.

To construct the desired wave function $\psi^+(\mathbf{q}, nE)$ analogous to (2.1) with (4.4) as the incident term, it is necessary to follow the two congruences of rays in (4.4) during the collision until they have become outgoing rays at large R. To do this we match an ingoing ray(s) of $\langle \mathbf{q}|nE^{\mathrm{i}}\rangle$ with one(s) of $\langle \mathbf{q}|n_2E^{\mathrm{i}}\rangle$ by finding the stationary phase value of $\int\langle n_2E^{\mathrm{i}}|\mathbf{q}\rangle\, d\mathbf{q}'\langle \mathbf{q}|nE^{\mathrm{i}}\rangle$. (The $\mathbf{q}'$ indicates integration at a fixed large R.) The stationary phasing serves to match a $\mathbf{p}(\mathbf{q})$ in $|nE^{\mathrm{i}}\rangle$ with one in $|n_sE^{\mathrm{i}}\rangle$ and so provide a smooth trajectory to the q-b state. The outgoing ray(s) emerge as $\langle \mathbf{q}|n_2E^{\mathrm{f}}\rangle$. Thus, the rays lead from the initial state nE to a congruence in the q-b state. Then, from another congruence in the q-b state they go out to some $\mathbf{q}$ at large R. Upon summing the contributions from all q-b states and including the contribution (if any) from any

direct collision trajectories not involved in the caustics of fig. 3 ($\langle \mathbf{q}|nE^+\rangle_d$) one obtains

$$\psi^+(\mathbf{q}, nE) \equiv \langle \mathbf{q}|nE^+\rangle = \langle \mathbf{q}|nE^i\rangle + \langle \mathbf{q}|nE^+\rangle_d + \sum_{n_2} \langle \mathbf{q}|n_2E^f\rangle\langle n_2E^i|nE^i\rangle, \tag{4.6}$$

where the first term is the incident term, as in (2.1), and $\langle n_2E^i|nE^i\rangle$ denotes the stationary phase value of $\int\langle n_2E^i|\mathbf{q}\rangle\, d\mathbf{q}'\,\langle \mathbf{q}|nE^i\rangle$.

Comparison of eqn (2.6) and (4.6) shows that

$$-S_{mn} = \langle mE^f|nE^+\rangle_d + \sum_{n_2} \langle mE^f|n_2E^f\rangle\langle n_2E^i|nE^i\rangle, \tag{4.7}$$

where $\langle mE^f|n_2E^f\rangle$ is obtained by stationary phasing $\int\langle mE^f|\mathbf{q}\rangle\, d\mathbf{q}'\langle \mathbf{q}|n_2E^f\rangle$. The latter also serves to match an outgoing ray(s) in $\langle \mathbf{q}|n_2E^f\rangle$ with one(s) in $\langle \mathbf{q}|mE^f\rangle$.

Eqn (4.1)-(4.5) yield (after some manipulation related to that in eqn (7) of ref. (15))

$$\langle n_2E^i|nE^i\rangle = \beta_{ns} \exp\{i(\delta_{rs} - \tfrac{1}{2}\phi_s - \tfrac{1}{2}\pi)\}, \tag{4.8}$$

where

$$\beta_{ns} = \tfrac{1}{2} \sum_{\gamma=II,IV} |i\partial w_2^\gamma/\partial n|^{\frac{1}{2}} \exp\{i[F_4^\gamma + \tfrac{1}{2}(l_n + \tfrac{1}{2})\pi]\}, \tag{4.9}$$

and

$$F_4^\gamma = \int_{B_n}^{E} \mathbf{p}_\gamma\, d\mathbf{q} - k_nR = -\int \mathbf{q}\, d\mathbf{p}_\gamma \quad (\gamma = II, IV), \tag{4.10}$$

where w_2^γ is canonically conjugate to $2\pi n_2$, being equal to $\partial F_4^\gamma/\partial(2\pi n_2)$, and the integration over $\mathbf{p}_\gamma$ in (4.10) is over the path from B_n to E.

$$\langle mE^f|nE^f\rangle = \beta_{ms}^\dagger \exp\{i(\delta_{rs} - \tfrac{1}{2}\phi_s - \tfrac{1}{2}\pi)\}, \tag{4.11}$$

where

$$\beta_{ms}^\dagger = \tfrac{1}{2} \sum_{\gamma=I,III} |i\partial w_2^\gamma/\partial m|^{\frac{1}{2}} \exp\{i[F_4^\gamma + \tfrac{1}{2}(l_m + \tfrac{1}{2})\pi]\}, \tag{4.12}$$

and

$$F_4^\gamma = \int_{E}^{B_m} \mathbf{p}_\gamma\, d\mathbf{q} - k_mR = -\int \mathbf{q}\, d\mathbf{p}_\gamma \quad (\gamma = I, III). \tag{4.13}$$

The δ_{rs} in eqn (4.8) and (4.11) is given by [11]

$$\tan \delta_{rs} = \frac{[1+\exp\{-\theta_s\}]^{\frac{1}{2}} - 1}{[1+\exp\{-\theta_s\}]^{\frac{1}{2}} + 1} \tan\{\pi(n_1 + \tfrac{1}{2}) - \tfrac{1}{2}\phi_s\}, \tag{4.14}$$

and, when EF and BC are real caustics,

$$\theta_s = \left|\oint_{C_3} \mathbf{p}\, d\mathbf{q}\right|. \tag{4.15}$$

C_3 is a contour encircling BC and EF. ϕ_s, a function of θ_s given in ref. (11), is close to zero unless the system is near the top of the barrier between BC and EF. θ_s is given by a related equation [11] when BC and EF are complex caustics.

The exponential, $\exp\{\}$, in (4.8) can be written as $(\exp\{\}-1)+1$ and, it can be shown, that stationary phase value of $\Sigma_{n_2}\beta_{ms}^\dagger\beta_{ns}$ has the same form as (2.11). It constitutes contribution from the direct collision trajectory involving reflection from caustic EF. If the sum of this contribution and of S_{mn}^d is written as S_{mn}^0, eqn (4.7), (4.8) and (4.11) yield

$$S_{mn} = S_{mn}^0 - \sum{}' \beta_{ms}^\dagger\beta_{ns}[(\exp\{2i\delta_{rs} - i\phi_s\}) - 1], \tag{4.16}$$

where the sum over s denotes the sum over n_2 (at the given E). If the exponent is expanded about $E-E_s$ one obtains [11]

$$S_{mn} = S^0_{mn} - \sum_s \beta^\dagger_{ms}\beta_{ns}\Gamma_s/(E-E_s+i\Gamma_s/2), \tag{4.17}$$

where the E_s are the E's for which n_1 is an integer (when $\phi_s \approx 0$) and where Γ_s is given by eqn (24) of ref. (11). When $\exp\{-\theta_s\} \ll 1$, we have

$$\Gamma_s/\hbar \approx \nu_{1s}\exp\{-\theta_s\}, \tag{4.18}$$

where ν_{1s} is the frequency $\partial E/\partial(2\pi n_1)$ for the mode corresponding to n_1 in the q-b state s. $i\theta_s$ can be calculated as the difference of the $\oint \mathbf{p}\,d\mathbf{q}$ over a path (from any nE to any mE) which encircles caustic EF and one over a path which encircles both EF and BC. (The ends of the paths at large R are joined analytically, and care is taken to compare paths on the same ingoing branch γ.)

To apply eqn (4.16) or (4.17) in a form utilizing exact trajectories it is necessary to obtain the F_2 for the q-b state, as deduced from Section 3. From caustic BC one then calculates trajectories leading to the open channels. The usual analytic arguments [1, 2] at large R then yield the integrals in β_{ns} and $\beta^\dagger_{ms}$.*

5. DISCUSSION

Eqn (4.16) has the appropriate factorization property,[9] one which reflects the " loss of memory " of " indirect " collisions occurring in the q-b state. It also has the appropriate time-reversal symmetry of S_{mn}, since $\beta^\dagger$ is a time-reversed β.

When state $|n_2E\rangle$ couples strongly with some state, the β for that state will be close to and can be replaced by unity or evaluated by an integral expression (suitably expressed in terms of $\bar{w}$'s) used to obtain (4.8). The small β's can still be evaluated by the semiclassical expression (4.8) and (4.11). When the collision system is purely elastic, the sum over s reduces to a single term $\beta^\dagger_{ns}\beta_{ns}$ (= 1), and the formulation reduces to that [11] for elastic collisions, as it should.

One implication of (4.17) for purely classical calculations involving complexes may be noted. When the relevant Γ_s's are large, one may anticipate that classical trajectories will reasonably well reproduce the quantum dynamical behaviour. When, however, a relevant Γ_s is small one should, at least, exclude from such calculations certain trajectories—those for which an individual vibration associated with the Γ_s has, for any significant time, an energy substantially less than its zero-point energy. Otherwise the calculations could not approximate in this respect the corresponding quantum mechanical behaviour.

Some extensions and applications, computational and perturbative, will be described elsewhere.§ As in the case of direct collision trajectories some partial averaging [30] should serve to isolate aspects of the collision which are predominantly quantum mechanical.

* E.g., to calculate β_{ns} the analytic expression for $\mathbf{p}_\gamma(\mathbf{q})$ in state nE at large R is used to calculate $-\int \mathbf{q}\,d\mathbf{p}_\gamma$ from B_n to a point on the trajectory leading to BC. The $\mathbf{p}_\gamma(\mathbf{q})$ data for that trajectory are then employed, and the q-b $\mathbf{p}_\gamma(\mathbf{q})$ data are used to obtain the contribution to reach B. Subtraction of $i\theta_s/2$ then yields the value to reach E.

§ Eqn (4.3)-(4.13) refer, for simplicity, to a vibration-translation problem, but are readily extended to include rotational and orbital problems by including appropriate generating functions, functions which disappear in the second halves of (4.10) and (4.13). Certain $\frac{1}{2}\pi$ terms, arising from passage through vibrational turning-points, are also omitted for brevity.

APPENDIX

DERIVATION OF EQN (3.5) AND (3.6)

The path from A to D on any branch γ can be deformed to lie along the caustic AD. The component of $\mathbf{p}$ normal to AD is zero, and so (fig. 2) $\mathbf{p}_{\mathrm{I}} = \mathbf{p}_{\mathrm{IV}} = -\mathbf{p}_{\mathrm{II}} = -\mathbf{p}_{\mathrm{III}}$ on AD. The integral $\int \mathbf{p}_\gamma d\mathbf{q}$ from A to D for γ = I or IV thus equals that from D to A for γ = II or III. This fact is used in the comparison of the solution (3.2) and the corresponding one originating from D to show that the magnitude of the above integral equals $\pi(n_2+\frac{1}{2})$, whence $\oint \mathbf{p}\,d\mathbf{q}$ equals $2\pi(n_2+\frac{1}{2})$ if the cyclic path C_2 lies along AD.

To prove (3.5) one may suitably deform the above path, and to do this it is necessary to remove the multivaluedness of $\mathbf{p}$. While $\mathbf{p}$ (and hence ∇F_2) is a function of $\mathbf{q}$, one may introduce a Riemann surface on which it is single-valued.[20] As usual the pair of sheets which have the same $\mathbf{p}$ at a branch cut (caustic) are joined. When one does this at all caustics, one obtains for the Riemann surface a torus,[20] as in fig. 4, where the torus is an open "cylinder", whose rims are the "ellipse" passing through C and D and the one passing through A and B.

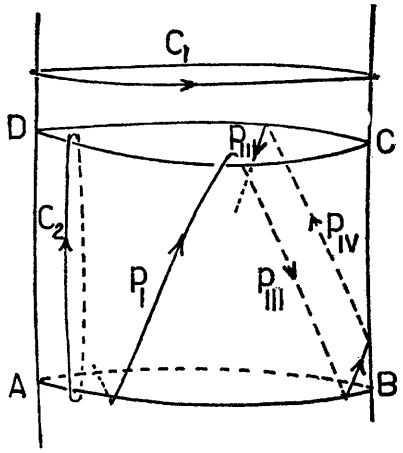

FIG. 4.—Riemann surface for the system in fig. 1 and 2. The two lines joining D to C coincide spatially, as do the two joining A and B. The congruences in fig. 1 and 2 are indicated, as are the cyclic paths C_2 and C_1 in eqn (3.5) and (3.6).

The momentum $\mathbf{p}(\mathbf{q})$ is now a (single-valued) analytic function of $\mathbf{q}$ on this surface, and so one may deform the contour C_2 for $\oint \mathbf{p}\,d\mathbf{q}$, which originally went from A to D and back to A along AD, to be any other equivalent cyclic C_2 path as indicated in fig. 4. Mathematically, this path is equivalent to the second half of (3.5). Eqn (3.6) is obtained similarly.

In three dimensions, points A and D lie at the corner of a cube, instead of a square, and AD lies along an edge. Once again all $\mathbf{p}_\gamma$'s are equal in magnitude on AD, since the components of $\mathbf{p}$ normal to the edge vanish. Thus, the preceding argument can be generalized. For an N-dimensional system, it leads to $\oint \mathbf{p}\,d\mathbf{q}$ equal to $2\pi(n_i+\frac{1}{2})$, for the N topologically independent paths C_i.

Fig. 2 is, essentially, a deformed square. An equilateral triangle has also been treated, by a different method.[20]

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